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(54) Title: CONTROLLED DEGRADATION COATINGS AND A METHOD FOR THEIR MANUFACTURE

(57) Abstract

A coating for a biodegradable article comprises a hydratable coating or a chemically or physically discontinuous coating. Imperfections in the coating, which may comprise pores in the coating, enable water to penetrate to the underlying surface of the water soluble article. The nature and extent of the imperfections permits the rate of penetration of the coating by water to be controlled. Alternatively, the coating is a hydratable coating which swells and tears on hydration to expose the underlying article to moisture. By these means, the article can be protected from premature dissolution during its normal working life, but will degrade on disposal to waste, when the surface coating will degrade to permit water to reach and dissolve the underlying article. Typically, the body of the article comprises water soluble, biodegradable polyvinyl alcohol or polyvinylalcohol/polyvinylacetate copolymer. Chemical/physical discontinuity may be achieved by over-coating a surface already covered with a physically flawed coating with a hydratable coating.



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CONTROLLED DEGRADATION COATINGS AND
A METHOD FOR THEIR MANUFACTURE

The present invention relates to controlled degradation coatings and in particular to
5 coatings for polyvinylalcohol and polyvinylalcohol/polyvinylacetate copolymers and to a
method for their manufacture.

Polyvinyl alcohol (PVA) and polyvinylalcohol/polyvinylacetate co-polymers (PVA/PVAc)
are materials which are subject to aqueous dissolution. Post dissolution, these materials
10 will readily biodegrade on exposure to bacteria present in the environment. These
polymers and their part degradation products and degradation products are non-toxic and
pose no risk of bio-accumulation or long term hazard to the environment, particularly when
the polymers are processed as described in Irish Patent No. S75746.

15 PVA and PVA/PVAc are capable of being processed into a wide variety of useful articles
by thermoplastic processes. Once an article has fulfilled its useful life, it is desirable that
when it is discarded to waste (landfill or similar), the article will rapidly dissolve and
subsequently biodegrade. The application of PVA and PVA/PVAc copolymers in the
manufacture of many types of articles is limited by the possibility of premature dissolution,
20 which may occur should the article become damp during its working life. Also, the article
may absorb atmospheric moisture, rendering it softer and mechanically weaker than
designed. There are also problems of handling by humans in that when PVA/PVAc co-
polymer materials absorb perspiration, they become sticky to the touch.

25 WO 92/01556 and WO 93/22125 disclose the manufacture of articles of coated PVA/PVAc
copolymers by layering or surrounding PVA/PVAc which is water soluble at 20°C with a
thin layer of PVA which is insoluble in water at 20°C. Thus an article may be
manufactured which would be protected from dissolution until its waterproofing insoluble
layer is breached. The copolymer and coating are disclosed as being co-extruded,
30 laminated or moulded, with or without an intervening filler layer.

US-A-5,196,247 discloses films of PVA co-extruded or heat laminated with thermoplastic
water insoluble polymers and co-polymers, such as polyethylene, polypropylene,
ethylvinyl acetate, ethyl methyl acrylate and ethyl acrylic acid.

35 GB 1,271,424 discloses a bed-pan liner consisting of 3 or 4 layers. The layers comprise a
water soluble or dispersible base layer, coated by a continuous water repellent layer with a

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- wax based flexible adhesive between. The bed pan liner should fully disintegrate within 5-10 seconds on immersion in water. EP 0589437A1 discloses a compostable disposable film manufactured by the coating of water soluble polymeric materials with a very thin layer of water insoluble surface coating materials such as polyvinylidene chloride with an intermediate adhesive or primer layer which may consist of polyesters or polyurethanes.

- 5 US-A-4,939,030 discloses a method for the manufacture of a film to retain the freshness of fruit by coating a PVA film with a thermoplastic film to form a laminate. The outer layer is pierced by pins to create holes of less than 30 microns to form a breathable outer layer
10 over a moisture absorbing inner layer such that the film does not have a moisture permeability lower than 100g/m²/24hr.

- 15 WO 92/15454 discloses a heat bonded laminate of PVA film with a film of polyethylene/polypropylene non-woven fibre. Similarly US-A-5,268,222 discloses a composite fabric of material which is water soluble at room temperature and a second PVA layer which is soluble above 140°F (60°C) and insoluble below 140°F, while US-A-5,500,281 discloses a 2 ply heat bonded laminate of 2-10% water soluble PVA non-woven fibres and an absorbent fibre web.
- 20 US-A-4,503,098 discloses a disposable film manufactured by the coating of water soluble polymeric materials with a layer of degradable water insoluble surface coating. The insoluble coating consists of 0.5-5 mils (13.2-130 micrometres) thickness of poly(beta-hydroxybutyrate), a dialkanoyl polymer or an ethylene polymer and the coating is susceptible to breakdown by sunlight or bacteria.
- 25 Irish Patent No. S71912 discloses that a PVA/PVAc co-polymeric article may be waterproofed by coating the surface with a phenoxy based surface coating to render it resistant to premature dissolution. A portion of the article may be left uncoated to permit a route by which it may ultimately undergo total dissolution. Alternatively, the entire
30 surface may be coated, in which case the article must be broken prior to disposal to expose the biodegradable co-polymer.
- 35 WO 93/22125 additionally discloses that a cast/co-extruded article with a cold water soluble inner core and a hot water soluble outer skin may be coated in part with an alcohol based flexographic ink to render the item additionally waterproof.

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GB 2,193,925A discloses the construction by bonded lamination of a multi-layered polyethylene web/PVA/PVA laminate. The composite sheet is designed for the rapid disintegration of both PVA layers leaving a residue of 19 micron thickness polyethylene web for disposal.

5

US-A-5,283,090 discloses a multi-layer laminated sheet for the construction of disposable sanitary items. The laminate consists of a water impermeable/water insoluble film bonded to one side of an absorbent water swellable layer with a water resistant layer applied to the other surface. The water resistant layer is formed by the application of a fluorine-containing or silicone-type water repellent resin dissolved in an organic solvent. Similarly US-A-5,674,578 discloses a laminate of a water soluble/water dispersible plasticised polyvinyl chloride and polyethylene oxide layer and a layer of a relatively weak water insoluble polymer or copolymer of vinylidene chloride, having a high resistance to liquid and gas.

10

GB 2,195,919A discloses a film for the construction of a disposable ostomy bag which is degradable by immersion in alkali solution (e.g. treatment in a pH 10 solution including triethanolamine and surfactants) then disposed of by flushing down the toilet. The bag is constructed of a three ply sheet of material; the central layer being PVA, the inner layer being a double coating of highly hydrophobic PVC/Acrylonitrile copolymer and the outer layer being carboxylated acrylic acid polymer which is substantively water resistant at neutral pH. On treatment with alkali the carboxylic acid outer coating breaks down and allows dissolution of the central sheet. The inner coating is considered to be of insufficient strength on its own and liable to tear and break-up on disposal down the toilet without

20

blocking the toilet. The description of the formation of the outer and inner layer indicates that they are a double coatings of 2 x 2.5 micron. Similarly US-A-5,277,898 discloses acidic acrylic coatings used in hair perm products, which can be removed under alkaline conditions. Also it discloses an acid soluble coating of alkali-treated shellac. The protective layers described may be applied to PVA. US-A-5,508,101 discloses a multi layered laminate of non-woven webs or films. The inner layer is water soluble and heat bonded on both sides with a web or film of alkali hydrolysable polymers, such that the whole article is dispersable in aqueous alkali.

25

The aforementioned processes, many by expensive co-extrusion or lamination techniques, seek to protect PVA articles during their working life by fully coating the item with non-degradable or slowly degradable materials and or materials which are non-hydrolysable under normal conditions. It is necessary that the article be physically broken, or that the

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- protective surface be pierced or hydrolysed under caustic or acidic conditions prior to disposal to permit the dissolution of the inner PVA core. Alternatively, the processes seek to leave some area of the PVA item uncoated by the protective layer to permit a route by which dissolution may occur on final disposal. The latter method may not fully protect a
5 PVA or PVA/PVAc article during its working life and may be regarded as complex in application and potentially expensive.

The present invention seeks to overcome the disadvantages of known coatings by providing a coating which permits degradation and dissolution of a coated article in a
10 controllable manner.

Accordingly, the present invention provides a water soluble article at least partially coated by a water resistant hydratable coating or a chemically and/or physically discontinuous surface coating which is susceptible to breakdown or penetration by water so that the
15 coating resists degradation on contact with or immersion in an aqueous medium under normal conditions which the article is likely to encounter during its useful working life, the coating being susceptible to eventual penetration and degradation by water on prolonged contact with or immersion of the article in an aqueous medium when the article is discarded to waste.

20 In one arrangement, the coating becomes hydrated on prolonged exposure to aqueous medium causing it to swell and tear, enabling water to contact the water soluble surface underlying the coating, the degradation of the coating being independent of the prevailing pH.

25 In another arrangement, the coating is formed with imperfections comprising microscopic discontinuities or pores which on prolonged exposure enable water to contact the surface underlying the coating.

30 Conveniently, the body of the articles comprises polyvinylalcohol polymer or polyvinyl-alcohol/polyvinylacetate copolymer. The rate of degradation of the coating may be controlled by selection of the thickness and/or physical and/or chemical structure of the coating. The coating includes single or blended surface coating resins having slight hydrophilic character or hydrophobic character. Most preferably, the coating includes
35 material having low or no environmental toxicity.

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- Single or blended acrylic resins may be used in the preparation of the coating, which may further include one or more plasticisers, waxes, surfactants and/or pigments or dyes.
- The coating includes a non-aqueous solvent selected from esters, ketones, alcohols, white spirit, chlorinated solvents, and aliphatic or aromatic solvent. Decoration of the coating may be achieved by conventional printing methods, including screen, flexographic and gravure printing. Conveniently, the coating is thermoplastic and permits the coated article or material to be welded.
- In one arrangement, the components of the surface coating are selected to permit the article or material to be used in food contact applications.
- In the case where the coating is a physically discontinuous one, the coating may be coated over by a further aqueous or organic solvent based resin, or by a heat or adhesive bonded layer to provide an additional dissolution resistant, modified surface for purposes of printing, adhesion, smoothness of finish or gloss, or further surface coating.
- In one arrangement, the coating is formed with imperfections comprising microscopic discontinuities or pores which on prolonged exposure enable water to contact the surface underlying the coating. In an alternative arrangement, the coating is chemically constituted so that it becomes hydrated on prolonged exposure to aqueous medium causing it to swell and/or tear, enabling water to contact the water soluble surface underlying the coating, irrespective of the prevailing pH.
- In either case, the degradation of the coating and the dissolution of the underlying article is pH independent. Under normal circumstances, the degradation will occur at or near neutral pH.
- By over-coating a coating having microscopic discontinuities with a coating which hydrates and tears on exposure to water, extra moisture resistance can be imparted to the article, whilst at the same time providing a surface which is non-porous and which can accept further overcoating for purposes of printing, obtaining a desired surface finish or texture, or the like.
- The body of the articles or material may comprise polyvinylalcohol polymer or polyvinyl-alcohol/ polyvinylacetate copolymer. The rate of degradation of the coating is controlled by selection of the thickness and/or physical and/or chemical structure of the coating. The

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- coating may include single or blended surface coating resins having slight hydrophilic character or hydrophobic character. The material used in manufacturing the coating preferably has low or no environmental toxicity.
- 5 The coating may include single or blended acrylic resin and one or more plasticisers, waxes and/or surfactants. It may further include a non-aqueous solvent selected from esters, ketones, alcohols, white spirit, chlorinated solvents, aliphatic or aromatic solvents. Also present may be a pigment or dye.
- 10 A coating according to the invention may be decorated by conventional printing methods, including screen, flexographic and gravure printing. Most preferably, the coating is thermoplastic and permits the coated article or material to be welded to itself or to another article or material. The components of the surface coating are conveniently selected to permit the article or material to be used in food contact applications.
- 15 The invention also provides a method of preparing a moisture resistant water soluble article, comprising at least partially coating a water soluble article with a coating material which includes single or blended surface coating resins having slight hydrophilic character or hydrophobic character, the coating being hydratable or being applied in such a way that it has chemical and/or physical discontinuities which render it susceptible to penetration by water so that on exposure to moisture conditions which are not encountered by the article during its normal useful working life but which are encountered when the article is discarded to waste, the coating degrades to permit water to contact and dissolve the article.
- 20
- 25 The present invention further provides a coating composition suitable for use as a water resistant hydratable coating or a chemically and/or physically discontinuous surface coating for a water soluble article, the composition comprising single or blended resins having slight hydrophilic character or hydrophobic character, the resultant coating when applied to an article being resistant to degradation by water on contact with or immersion in an aqueous medium under normal conditions which the article is likely to encounter during its useful working life and being susceptible to degradation on prolonged contact with or immersion in the aqueous medium when the article is discarded to waste, enabling water to contact and dissolve the article.
- 30
- 35 Thus, the present invention relates to an improved method for the protection of water soluble PVA and PVA/PVAc copolymer articles by surface coating with water resistant surface coatings, which protect the articles from moisture during their working life, yet

- degrade to expose the article to moisture once the article is discarded. The article may be a formed article or a film or web, or the like. Once the article is exposed to moisture, it dissolves and the solute degrades in the environment.
- 5 Typically, the surface coatings are manufactured from polymeric resin materials (e.g. acrylic resins). The resins can be dissolved in one or more, or blends of non-aqueous solvents, including esters, ketones, alcohols, white spirits, chlorinated solvents or aromatics. Non-toxic or low toxicity solvents are preferred.
- 10 The control of degradation characteristics of these discontinuous surface coatings is achieved by chemical and/or physical weakness being incorporated into the coating by design, i.e. through choice of the type, and quantities of resins and/or solvent components and/or additives used.
- 15 For the purpose of this specification the following terms have the meaning defined below:-
- Resins or blends of resins which are soluble in non-aqueous solvents yet contain polar moieties or moieties which may possess an affinity for water (e.g. acrylic polymers containing polar hydrophilic pendant groups, such as free carboxylic acids groups), are 20 termed "slightly hydrophilic resins". Resins which contain no polar moieties are termed "hydrophobic resins".
- Surface coatings with designed chemical susceptibility to degradation by moisture may be manufactured from slightly hydrophilic resins, or blends of slightly hydrophilic resins or 25 hydrophobic resins.
- Surface coatings with designed physical imperfections may be manufactured from slightly hydrophilic resins, or blends of slightly hydrophilic resins and hydrophobic resins, or hydrophobic resins. The occurrence of the size and number of physical imperfections can 30 be regulated by agents which control film formation, e.g. solvents, plasticisers and solvent modifiers.
- Such coatings can be used fully to coat the PVA/PVAc article and will resist full immersion in water, and in some cases survive total immersion for several hours, thereby 35 rendering PVA/PVAc products practical for many applications. The limited nature of the water resistance permits the plastic articles ultimately to dissolve on disposal and subsequently biodegrade.

Any conventional surface coating means, including dipping, spraying, smearing, painting, printing, etc, may be used to apply the coating to the article.

- 5 The present invention also relates to the manufacture of surface coating systems which permit control of the rate of breakdown of the surface coating by the blending of resins with differing degrees of hydrophobic and slight hydrophilic character. The presence of the hydrophilic components in a largely hydrophobic surface coating provides zones of weakness, where moisture can cause breakdown of the coating permitting water to
- 10 penetrate to the PVA or PVA/PVAc material beneath the coating layer. The greater the slight hydrophilic nature of the resin system the faster will be the rate of breakdown.

The present invention also relates to surface coated articles in which the thickness of the applied surface coating is controlled to enable the rate of penetration or breakdown of the surface coating to be controlled. The thinner the coating applied the faster would be the breakdown. The present invention also relates to surface coated articles having discontinuities or imperfections in the surface coating to enable the rate of penetration or breakdown of the surface coating to be controlled. The less perfect is the coating film formation the faster would be the breakdown. Such surface coatings may be made with

- 15 blends of resins with differing degrees of hydrophobic and slightly hydrophilic character, or be made with single resins with hydrophobic character or made with single resins of slightly hydrophilic character.
- 20

Where a surface coating is wholly made from a resin of hydrophobic character, the depth of surface covering of the PVA/PVAc article is controlled to permit the occurrence of microscopic flaws (or pores). This renders the material highly durable in moisture sensitive applications, yet permits a route for the ultimate breakdown when the article is discarded.

- 25
- 30 By the incorporation of one or more plasticisers into the surface coating, the coating may be imparted sufficient flexibility to offer good adhesion to plasticised compounded PVA/PVAc which can be a relatively soft plastic. The presence of the plasticisers also serves to aid moisture resistance. Also the presence of a plasticiser aids the ultimate breakdown of the surface coating residue.

35 The surface coating plasticiser may be (a) any C1 to C10 mono-, di- or tri- ester of adipic acid, azelaic acid, phthalic acid, trimellitic acid or citric acid or (b) any mono-, di- or tri-

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- C1 to C10 carboxylic acid esters of glycerol, propylene glycol, 1,3-propanediol, ethylene glycol, tri-alkyl citrate ester or (c) any blend of (a) and (b). Materials which are non-toxic or of low toxicity, and with low migration properties are preferred.
- 5 The surface coating may include a wax material (eg Ceraflour waxes of BYK Cera) for added water resistance and improved anti-scratch properties. Also, if desired, surface active agents may be employed to assist wetting on application.
- Solvent modifiers may be included in the coating to control the rate of solvent evaporation, thereby yielding improved coating film formation and by implication effecting the occurrence of flaws (or pores) in the surface coating. Such modifiers include propylene glycol, 1,3-propanediol, ethylene glycol or any C1 to C4 mono- or di- ethers, or mono- or di- esters of the aforementioned.
- 10 A coated surface may be decorated by conventional means, e.g. Flexographic and Gravure printing inks. Also it may be coloured by pigments or dyes. The components of the surface coating may be chosen to permit varying degrees of gloss or matt finish.
- The surface coating may be thermoplastic in nature to permit heat sealing systems to be applied, such that coated articles or materials may be welded, e.g. to form bags from coated film materials.
- 15 The components of the surface coating may be chosen to permit a coated article to be used for food contact applications.
- 20 The size and distribution of the physical discontinuities can be controlled by the appropriate selection of resins or resin blends and in this way, the dissolution characteristics of the coated article may be controlled.
- 25 Hydrophobic resins suitable for use in the invention include
- BMA copolymers (eg, NeoCryl B-842 of Zeneca Resins)
 - IBMA copolymers (eg, NeoCryl B-875 of Zeneca Resins)
 - Polyvinyl Chloride and its copolymer (eg Vinylite VMCH of Union Carbide)
 - 30 - Phenoxy resins (eg PKHH-MM of B&K Resins/Phenoxy Inc.)
 - Nitrocellulose (eg DHX 8/13 of ICI Explosives)
 - Cellulose Acetate resins

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- Ethyl Cellulose resins
- Polyester resins
- Polyurethane resins
- Any IBMA, BMA, MMA, EMA, BA, vinyl ester, styrenic, maleic acid, butadiene,
5 ethylene, propylene polymer or co-polymer of any of the aforementioned materials with
an Acid value less than 1mg KOH per gram.

Slightly Hydrophilic Resins useful in the invention include:

- 10 - IBMA Copolymers (eg, NeoCryl 862 of Zeneca Resins)
- Styrene/IBMA copolymers (eg, NeoCryl 880 of Zeneca Resins)
- Carboxylated acrylic resins (eg; Surcol 836 or Surcol 860 of Allied Colloids)
- Any IBMA, BMA, MMA, EMA, BA, vinyl ester, styrenic, maleic acid, butadiene,
ethylene, propylene polymer or co-polymer of any of the aforementioned materials with
15 an Acid value less than 200 or greater than or equal to 1mg KOH per gram.

The above lists are not limiting and other suitable materials or combinations of materials will suggest themselves to the skilled person.

- 20 The present invention also relates to the preparation of PVA and PVA/PVAc surface coatings from acrylic based polymers. Acrylic based polymeric materials are preferred as they are potentially biodegradable and present a low risk to the environment.

Given that the protection of a water soluble article by a physically discontinuous water
25 resistant coating can impart sufficient water resistance so that the article may be over-coated, even by an aqueous based resin coating, without risk of dissolving the articles, the present invention also relates to the subsequent over-coating of the physically discontinuous coating. The over-coating may comprise one or more layers of aqueous and/or organic solvent based surface coatings, and/or covering the same by a heat bonded
30 or adhesive bonded layer which may provide additional dissolution resistance or may modify the surface printing properties, adhesion properties, anti-blocking properties, smoothness of finish or gloss characteristics, or permit further surface coating. In general the subsequent coatings will have a faster rate of breakdown than the discontinuous layer. Such a composite film as described above would appear as a physically continuous film but
35 contain zones of greater and lesser resistance to hydration and hence the article would be protected by a combined chemically and physically discontinuous coating.

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The invention will now be described more particularly with reference to the following non-limiting examples.

Preparation of Surface Coatings

5

Solvents; Ethyl acetate (50 parts by weight (PBW)) and isopropanol (14 PBW) were combined. Resins; NeoCryl B-842 (0-30 PBW) and Surcol(R) 836 (30-0 PBW) were added with stirring. After complete dissolution additives; Dowinol (1.5 PBW) and plasticiser Bisoflex(R) DOA (4.5 PBW) (total 100 PBW) were added and the varnish 10 mixed until homogeneous. The compositions of five exemplary formulations A to E are shown in Table 1.

'NeoCryl' is a Trademark of Zeneca Resins; 'Surcol' is a Trademark of Allied Colloids; 'Bisoflex' is a Trademark of British Petroleum Co. and used under license by International 15 Speciality Chemicals; 'Dowinol' is a Trademark of Dow Chemicals)

TABLE 1

	Example	Resin Ratio	
		NeoCryl B-842	Surcol 836
20	A	30	0
	B	25	5
	C	20	10
25	D	15	15
	E	0	30

Coatings indicated Examples A to E were made as above. Samples of A to E were drawn down with a K-Bar to give a 4 micron wet coating on Polyethylene and PVA/PVAc film.

30

Coated Film Results: - Films coated with formulations A-D had good retention of strength on light exposure to moisture, whereas uncoated film control rapidly absorbed moisture and reverted to a semi-liquid paste. Formulations A-C had good adhesion to PVA/PVAc film on stretching and creasing with A and B having the best performance. Formulations D 35 and E tended to have less flexibility and form microscopic cracks on creasing and stretching, which lead to mechanical weakness on immersion in water.

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- Coatings A to E above were diluted 1:1 with ethyl acetate and a test PVA/PVAc injection moulding was fully immersed into the resin and allowed to dry. The test moulding was a thimble shaped injection moulding of approximate dimensions; 43mm high, 16mm dia, wall thickness 1mm, base thickness 5mm and weighing approximately 3 gram. The
- 5 thickness of the dry surface coatings was typically 3 to 5 microns. The dried coated mouldings were immersed in 500 ml of pure water and the dissolution observed against an uncoated test moulding as control.

Coated Test Moulding Results:

10

The characteristics shown by the article coated with the example A to E formulations, by comparison with an untreated control sample are shown in Table 2.

TABLE 2

15

Example Dissolution Properties of Test Mounting

20

Control After 5 minutes immersion, the TM surface visibly gelled.
10 minutes TM was visibly swollen with dissolution evident.
1 hour the wall of the TM was part dissolved and distorted.
20 hours the wall of the TM has totally dissolved with the base remaining as a gelatinous plug of material.
36 hours complete dissolution of TM.

25

A After 30 minutes some puckering of the surface coating near mechanical flaws.
1 hour slight increase size of pucker near surface flaws.
1 hour 30 minutes, some surface coating breakdown.
2 hours de-lamination. TM dissolves as control leaving a thin, friable residue of flexible clear film.

30

B After 30 minutes some puckering of the surface coating.
1 hour some surface coating breakdown.
1 hour 30 minutes, surface coating breakdown and delamination. TM dissolves as control leaving a thin, friable residue of flexible clear film.

35

C After 30 minutes some puckering of the surface coating.
1 hour slight opacity observed in surface coating, with slight coating breakdown.
1 hour 30 minutes, surface coating breakdown and de-lamination. TM dissolves as control leaving a thin, friable residue of slightly opaque film.

40

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- D After 5 minutes some puckering of the surface coating.
30 minutes slight opacity observed in surface coating with coating breakdown.
1 hour significant de-lamination. TM dissolves as control leaving a thin, very friable residue of opaque film.
- E After 5 minutes some puckering and breaking of the surface coating.
15 minutes surface coating breakdown and de-lamination. TM dissolves as control leaving dispersed particles of a thin friable residue of opaque film.

10

Microscopic Analysis

Flat, circular test plaques were coated as indicated above. The dried surface coated plaques all appear clear and even to the naked eye. The surface coatings were then examined under 15 a microscope, (an Olympus XA40 x 100 magnification) to reveal the coatings micro-structure. The results are shown in the accompanying Figures 1 to 6, which show respectively an untreated control, Example A and Example B (Figures 1 to 3 respectively), Example C (Figures 4 and 5) and Example D (Figure 6).

20 The illustrations, Figures 1 to 6 represent a region 575×435 micron (10^{-6} m).

The surface of the control (Figure 1) indicates a flat surface scored by fine straight lines. These details are attributed to fine linear abrasions on the mould of the test plaque.

25 Example A (Figure 2) illustrates a smoother surface than the control, where the test plaque abrasions have been covered. There are numerous fine pores or depressions (1-7 micron in diameter) randomly distributed over the surface coating at an approximate number of 2-300 per mm^2 .

30 Example B (Figure 3) illustrates a gently undulating surface, where the test plaque abrasions have been covered. There are numerous fine pores or depressions (1-15 micron in diameter) distributed in clusters over the surface, being typically situated in depressions in the undulating surface coating. The approximate number of pores is 3-400 per mm^2 .

35 Example C (Figures 4 and 5) illustrates a gently undulating surface, where the test plaque abrasions have been covered. There are numerous round or ovate pores or depressions (30-100 micron in diameter) distributed evenly over the surface. The approximate number of pores being 34-45 per mm^2 .

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- Example D (Figure 6) illustrates an undulating surface where numerous ridges have formed, roughly running parallel and 2-300 micron apart. The test plaque abrasions have been covered. Though distributed evenly over the surface, the pores or depressions have increased in size (typically 100-150 micron in diameter) and are more irregular in shape,
- 5 with some forming channels of up to 500 micron length. The approximate number of pores being 5-10 per mm². In these larger pores, there are numerous smaller pores or depressions (1-20 micron in diameter).

It will of course be understood that the invention is not limited to the specific details
10 described herein, which are given by way of example only, and that various modifications and alterations are possible within the scope of the invention as defined in the appended claims.

CLAIMS:

1. A water soluble article at least partially coated by a water resistant hydratable coating or a chemically and/or physically discontinuous surface coating which is
5 susceptible to breakdown or penetration by water so that the coating resists degradation on contact with or immersion in an aqueous medium under normal conditions which the article is likely to encounter during its useful working life, the coating being susceptible to eventual penetration and degradation by water on prolonged contact with or immersion of the article in an aqueous medium when the article is discarded to waste.
- 10 2. An article according to Claim 1, in which the coating becomes hydrated on prolonged exposure to aqueous medium causing it to swell and tear, enabling water to contact the water soluble surface underlying the coating, the degradation of the coating being independent of the prevailing pH.
- 15 3. An article according to Claim 1, in which the coating is formed with imperfections comprising microscopic discontinuities or pores which on prolonged exposure enable water to contact the surface underlying the coating.
- 20 4. An article according to Claim 2 or Claim 3, in which the body of the articles comprises polyvinylalcohol polymer or polyvinyl-alcohol/polyvinylacetate copolymer.
- 25 5. An article according to any preceding claim in which the rate of degradation of the coating is controlled by selection of the thickness and/or physical and/or chemical structure of the coating.
- 30 6. An article according to any of the preceding claims, in which the coating includes single or blended surface coating resins having slight hydrophilic character or hydrophobic character.
7. An article according to any of the preceding claims, in which the coating includes material having low or no environmental toxicity.
- 35 8. An article according to any of Claims 1 to 6, in which the coating includes single or blended acrylic resin.

9. An article according to any preceding claim, in which the coating includes one or more plasticisers.
10. An article according to any preceding claim, in which the coating includes one or 5 more waxes and/or surfactants.
11. An article according to any preceding claim, in which the coating includes a non-aqueous solvent selected from esters, ketones, alcohols, white spirit, chlorinated solvents, and aliphatic or aromatic solvent.
- 10 12. An article according to any preceding claim, in which the coating includes a pigment or dye.
13. An article according to any preceding claim, in which the coating is decorated by 15 conventional printing methods, including screen, flexographic and gravure printing.
14. An article according to any preceding claim, in which the coating is thermoplastic and permits the coated article or material to be welded.
- 20 15. An article according to any preceding claim, in which the components of the surface coating are selected to permit the article or material to be used in food contact applications.
- 25 16. An article according to any of Claims 3 to 15, in which the discontinuous coating is coated over by a further aqueous or organic solvent based resin, or by a heat or adhesive bonded layer to provide an additional dissolution resistant, modified surface for purposes of printing, adhesion, smoothness of finish or gloss, or further surface coating.
- 30 17. A method of preparing a moisture resistant water soluble article, comprising at least partially coating a water soluble article with a coating material which includes single or blended surface coating resins having slight hydrophilic character or hydrophobic character, the coating being hydratable or being applied in such a way that it has chemical and/or physical discontinuities which render it susceptible to penetration by water so that on exposure to moisture conditions which are not encountered by the article during its 35 normal useful working life but which are encountered when the article is discarded to waste, the coating degrades to permit water to contact and dissolve the article.

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18. A method according to Claim 17, including adjusting the thickness and/or physical and/or chemical structure of the coating to control its rate of degradation on exposure to water.
- 5 19. A coating composition suitable for use as a water resistant hydratable coating or a chemically and/or physically discontinuous surface coating for a water soluble article, the composition comprising single or blended resins having slight hydrophilic character or hydrophobic character, the resultant coating when applied to an article being resistant to degradation by water on contact with or immersion in an aqueous medium under normal
10 conditions which the article is likely to encounter during its useful working life and being susceptible to degradation on prolonged contact with or immersion in the aqueous medium when the article is discarded to waste, enabling water to contact and dissolve the article.

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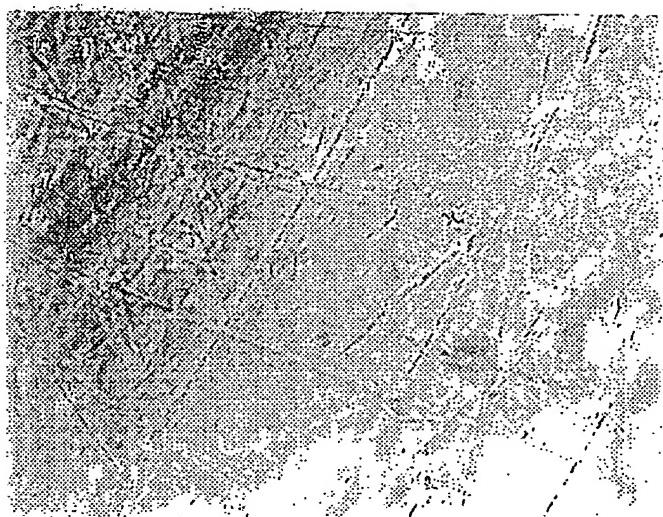


FIGURE 1

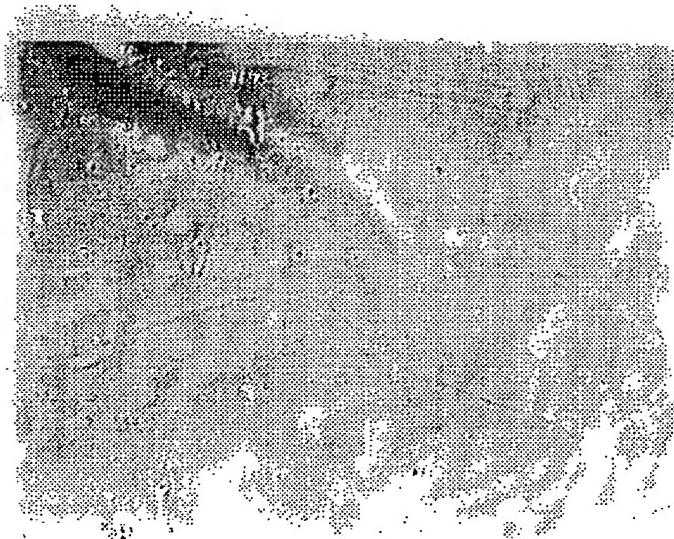


FIGURE 2

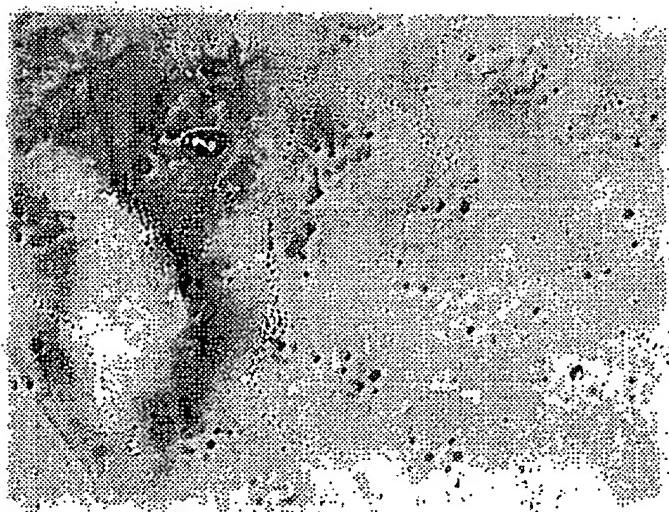


FIGURE 3

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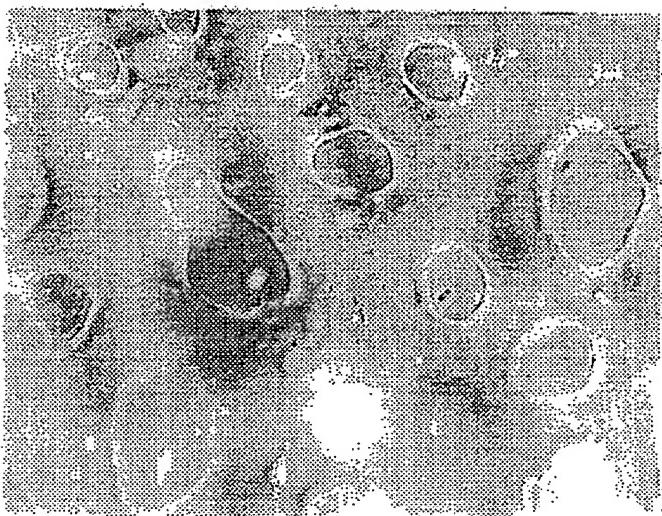


FIGURE 4

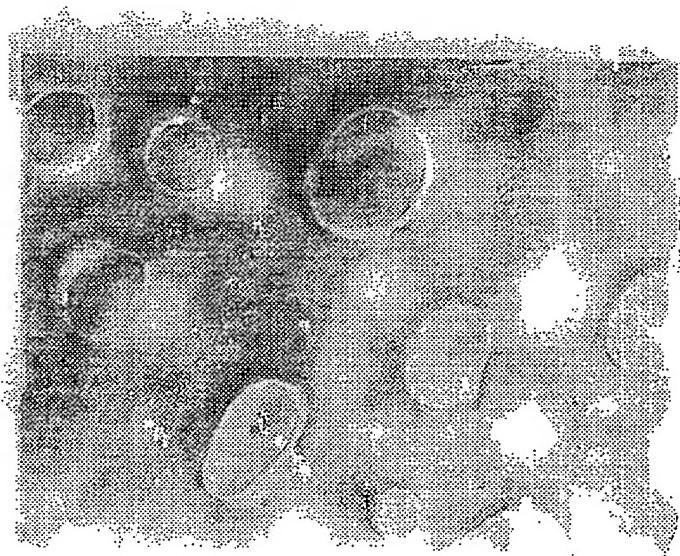


FIGURE 5



FIGURE 6

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/IE 98/00028

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J7/04 //C08L29:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 17202 A (COURTAULDS PACKAGING LIMITED) 14 November 1991 see claims 1-12 see examples 1,2 see page 2, paragraph 4 - page 5, line 19 see page 6, paragraph 4 ---	1-4, 6-12,14, 17-19
X	WO 93 22125 A (ENVIRONMENTAL POLYMERS LIMITED) 11 November 1993 cited in the application see claims 1,10-15,17-23 ---	1,13
A	US 4 372 311 A (J.E. POTTS) 8 February 1983 see claims 1,2,18-20 see column 2, line 14 - line 40 ---	1,4 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

6 August 1998

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12/08/1998

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INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/IE 98/00028

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 503 098 A (J.E. POTTS) 5 March 1985 cited in the application see claims 1,2,7 ---	17-19
A	EP 0 703 265 A (HOECHST AKTIENGESELLSCHAFT) 27 March 1996	1,2,6-8, 17 19
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